

The Carbonyl Group Frequency. Part V.¹ Alkyl Formates

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The low carbonyl frequency of alkyl formates is not attributable to substituent polar effects. Calculations for a simplified model and comparison with other carbonyl compounds suggest it may arise from vibrational perturbations due to the presence of the hydrogen substituent, notably those due to the low mass and large coupling effects. The main carbonyl band is accompanied by a weaker band at higher frequency; this is assigned to the less stable *s-cis* isomer.

REPLACEMENT of the alkyl groups of acetone by more electronegative substituents raises the frequency of the carbonyl group vibration.² Thus both acetaldehyde and methyl acetate have higher carbonyl frequencies³ than acetone. In many carbonyl compounds the effects of multiple substitution can be treated additively² and useful empirical rules for the evaluation of carbonyl frequencies are available.⁴ In this respect the simple alkyl formates are apparently anomalous since their carbonyl frequencies are lower than those of the corresponding acetates.³ This observation does not lend itself to simple interpretation in terms of substituent polar effects. In an attempt to resolve the anomaly the spectra of a range of simple alkyl formates have been measured for a range of solvents and the in-plane skeletal vibrations of methyl formate analysed in terms of a simple model.

EXPERIMENTAL

t-Butyl formate was prepared from t-butanol (100 g), formic acid (50 ml), and acetic anhydride (100 ml). The product, b.p. 80–86°, was a mixture of esters which was cleanly fractionated by distillation through a spinning band column giving t-butyl formate,⁵ b.p. 83°, n_D^{22} 1.3791 and t-butyl acetate, b.p. 97°, n_D^{24} 1.3852. G.l.c. using an Apiezon L column and n.m.r. spectroscopy showed the purity of the formate to be >99% (using a PEGA column acetate and formate were not resolved).

Other formate esters were commercial samples which were dried and distilled before use. G.l.c. showed that in all cases the purity of the samples was >98%.

Solution spectra were measured using 0.1 mm cells for *ca.* 0.1M and 0.4M solutions in acetonitrile, dibutyl ether, dimethyl sulphoxide, dioxan, nitromethane, pyridine, and triethylamine; for other solvents 1.0 mm cells with *ca.* 0.01M and 0.04M solutions were used. At other than

* We were not able to reproduce the published spectrum of t-butyl formate in dimethyl sulphoxide showing a well defined inflection.⁹ Under our conditions the envelope of the carbonyl band is smooth but its asymmetric contour and increased half-band width indicate that it may embrace a second band.

¹ Part IV, J. S. Byrne, P. F. Jackson, and K. J. Morgan, *J.C.S. Perkin II*, 1972, 1291.

² L. J. Bellamy, 'The Infrared Spectra of Complex Molecules,' Methuen, London, 1957, chs. 9 and 11.

³ H. W. Thompson and P. Torkington, *J. Chem. Soc.*, 1945, 640; E. J. Hartwell, R. E. Richards, and H. W. Thompson, *ibid.*, 1948, 1436.

⁴ G. Eglinton, 'Physical Methods in Organic Chemistry,' ed. J. C. P. Schwarz, Oliver and Boyd, Edinburgh, 1964, ch. 3.

ambient temperatures a R.I.I.C. VLT-2 variable temperature unit was used. Vapours were examined in a 10 cm cell at pressures 5–20 mmHg, and at higher temperatures by the use of a R.I.I.C. CH 5 heated cell.

Spectra were recorded on a Perkin-Elmer model 225 spectrometer with dry air flushing. Calibration was by interpolation from external water vapour bands.⁶ Band locations were checked using a Du Pont 310 curve resolver and are believed to be accurate to better than ± 1 cm⁻¹ for main bands and ± 2 cm⁻¹ for inflections.

Vibrational frequencies were calculated for conventional **F** and **G** matrices⁷ using the following parameters: r_{C-H} 1.09, $r_{C=O}$ 1.22, r_{C-O} 1.37 Å,⁸ $k_{C=O}$ 10.92, k_{C-H} 4.66, k_{C-O} 4.8, $h_{HC=O}$ 0.49, h_{HC-O} 0.36, h_{OCO} 1.92, $f_{C=O,HC=O}$ 0.1, $f_{C-O,HC-O}$ 0.2, $f_{C-O,OCO}$ 0.1 m dyn Å⁻¹.

RESULTS

The carbonyl frequencies for alkyl formates as vapours and solutions are in Table 1. The band contours for the vapours exhibit well defined rotational structure and the quoted figures refer to the strong central branch. The main carbonyl band is accompanied by a second band which usually appears as a weak higher frequency inflection although a discrete peak is observed for solutions of some esters in nitromethane and acetonitrile; the relative intensity of the second band increases with temperature, with the bulk of the alkyl group and with the polarity of the solvent. The possibility that this band might be due to contamination by acetate from the use of the mixed anhydride was excluded by monitoring the samples by n.m.r. spectroscopy and g.l.c. analysis. Similar results have been reported for t-butyl formate in certain solvents by Oki *et al.**⁹ Where comparisons are possible the main carbonyl bands are generally in good agreement with those reported previously.^{3,9,10}

In-plane vibrational frequencies calculated for a simple tetra-atomic model (I) are in Table 2. This model is

⁵ W. D. Closson and P. Haugh, *J. Amer. Chem. Soc.*, 1964, **86**, 2384.

⁶ I.U.P.A.C. Tables of Wavelengths for the Calibration of Infrared Spectrometers, Butterworths, London, 1961.

⁷ E. B. Wilson, J. C. Decius, and P. C. Cross, 'Molecular Vibrations,' McGraw-Hill, New York, 1955.

⁸ Tables of Interatomic Distances, *Chem. Soc. Special Publ.*, Nos. 11 and 18, 1958 and 1965.

⁹ M. Oki and H. Nakanishi, *Bull. Chem. Soc. Japan*, 1970, **43**, 2558.

¹⁰ H. W. Thompson and D. A. Jameson, *Spectrochim. Acta*, 1958, **13**, 236; A. R. Katritzky, J. M. Lagowski, and J. A. T. Beard, *ibid.*, 1960, **16**, 964; R. Heess and H. Kriegsmann, *ibid.*, 1968, **24**, 2121.

TABLE 1
Carbonyl group frequencies (cm^{-1}) of alkyl formates ^a

Vapour Solvent	HCO_2Me		HCO_2Et		HCO_2Pr		HCO_2Bu		HCO_2Pr^t		HCO_2Bu^t	
	(1796)	1754.5	(1795.5)	1750	(1794.5)	1751	(1793.5)	1750.5	1787.5	1746.5	(1778)	1744
C_6H_{12}	(1774)	1740	(1768)	1736	(1768.5)	1736	(1768.5)	1736	(1766.5)	1732.5	(1754)	1732
NEt_3	(1769)	1737.5	(1765)	1735	(1763.5)	1735.5	(1760.5)	1735.5	(1758.5)	1731.5	(1749)	1729.5
Bu_2O	(1768)	1736.5	(1763)	1733	(1763)	1733.5	(1760.5)	1733	(1758)	1729	(1750)	1728.5
CCl_4	(1768)	1734.5	(1758)	1730.5	(1759.5)	1731	(1758)	1730.5	(1757)	1727	(1746)	1726
CS_2	(1762.5)	1733	(1757)	1729	(1756.5)	1729.5	(1757)	1729	(1753)	1725.5	(1742.5)	1724.5
Dioxan	(1755.5)	1727.5	(1750.5)	1724	(1750)	1724	(1751)	1724	(1748.5)	1720.5	(1735.5)	1720
MeCN	(1750.5)	1727	1747.5	1723	1745	1723	1746	1722.5	1742	1719	(1731.5)	1718.5
Pyridine	(1752)	1726	(1746.5)	1722	(1747.5)	1722.5	(1747.5)	1722	(1744)	1719		1718.5
MeNO_2	(1748.5)	1726	(1746)	1721.5	(1745.5)	1722	(1744)	1721.5	1741.5	1718	(1731)	1717.5
CH_2Cl_2	(1753.5)	1727	(1747.5)	1722	(1747)	1722.5	(1747)	1722	1746	1718.5	(1733.5)	1718
CHCl_3	(1750.5)	1726	(1748)	1721	(1748)	1721.5	(1748)	1721.5	(1744.5)	1717		1717
CHBr_3	(1751)	1722	(1745.5)	1717.5	(1745.5)	1718	(1745.5)	1718	(1741.5)	1714		1714
Me_2SO	(1745.5)	1718.5	(1741.5)	1715.5	(1741)	1716	(1739.5)	1715.5	(1736.5)	1712		1714
m^b	1.61	0.99	1.63	0.98	1.66	1.01	1.69	0.99	1.62	0.97	1.66	0.88

^a Frequencies in brackets indicate points of inflection. ^b Gradient of $\nu = m\nu_{\text{MeOAc}} + d$.

arbitrary in that the C-O stretching constant was set at the value used previously for methyl acetate ($4.8 \text{ mdyn } \text{Å}^{-1}$); ¹¹

formate changing only the value m_{H} in the **G** matrix shows reasonable agreement with the observed frequencies (Table 2).

TABLE 2

Frequencies (cm^{-1}) for in-plane skeletal vibrations of methyl formate

	HCO_2Me		DCO_2Me	
	Obs. ²¹	Calc.	Obs. ²⁴	Calc.
C-H Stretch	2943	2943	2216	2233
C=O Stretch	1754	1754	1712 *	1707
C-H Bend	1371	1376	1048	959
C-O Stretch	1207	1207	1213	1238
OCO Bend	767	759	762	758

* See Discussion section.

the C-H stretching constant is determined directly by the vibrational frequency and the other constants were adjusted

DISCUSSION

The variation in carbonyl group frequency with substitution has frequently been described in terms of the electronic effects of substituents on the contributions of canonical forms (II) and (III).²⁻⁴ This may be expressed quantitatively in terms of linear correlations with polar substituent constants.¹² Within the series of simple aliphatic esters there is good correlation¹³ of the group frequency with the polar substituent constants (σ^*) for alkyl substituents in both acyl and alkoxy-groups, $\nu_{\text{CO}}^{\text{vap}} \simeq 50\Sigma\sigma^* + 1770 \text{ cm}^{-1}$. For formates the effects on the carbonyl frequency of changes in the alkoxy alkyl group fit a similar equation, $\nu_{\text{CO}}^{\text{vap}} \simeq$

TABLE 3

Effect on the carbonyl frequency of changes in structural and vibrational parameters of some simple models

	Me_2CO	MeCO_2Me	$\Delta\nu_{\text{C=O}}$	Me_2CHO	HCO_2Me	$\Delta\nu_{\text{C=O}}$	Me_2CO	MeCHO	$\Delta\nu_{\text{C=O}}$	MeCO_2Me	HCO_2Me	$\Delta\nu_{\text{C=O}}$
	Force constants ^a		(cm^{-1})	Force constants		(cm^{-1})	Force constants		(cm^{-1})	Force constants		(cm^{-1})
			1			-2			-42			-33
Changes of mass and geometry:												
Changes in force constant												
$k_{\text{C=O}}$	10.42	10.44	2	11.95	10.92	-69	10.42	11.95	103	10.44	10.92	32
$k_{\text{C-O}}$	4.0	4.8	6	4.0	4.8	11						
$k_{\text{C-O}} \rightarrow k_{\text{C-H}}$							4.0	4.3	3	4.0	4.66	0
$k_{\text{CO=O}} \rightarrow k_{\text{OCO}}$	0.6	1.4	22	0.7	1.92	16						
$k_{\text{CCO}} \rightarrow k_{\text{CC-O}}$	0.45	0.35	-10									
$k_{\text{HCC}} \rightarrow k_{\text{HC-O}}$				0.3	0.36	9						
$k_{\text{CCO}} \rightarrow k_{\text{HCC}}$							0.45	0.3	-14			
$k_{\text{CO=O}} \rightarrow k_{\text{HC-O}}$							0.6	0.57	0	0.43	0.49	10
$k_{\text{CO-O}} \rightarrow k_{\text{HC-O}}$										0.35	0.36	3
$k_{\text{CO=O}}$	0.6	0.43	-2	0.57	0.49	-8	0.6	0.7	2			
$k_{\text{HC=O}}$										1.4	1.92	4
k_{OCO}												-36*
Changes in interaction constants:			17 ^b			51 ^c			-44 ^d			-20
Total frequency change:			36			8			8			

^a $\text{mdyn } \text{Å}^{-1}$. Force constants for $\text{Me}_2\text{CO}, \text{MeCHO}$ taken from ref. 1 and for MeCO_2Me from ref. 11. ^b $f_{\text{CC,CC}} \rightarrow f_{\text{CCO,CO-O}}, 10$; $f_{\text{CO,OCO}} 7 \text{ cm}^{-1}$. ^c $f_{\text{CO,HC=O}}, 33$; $f_{\text{CO,CCO}} \rightarrow f_{\text{CO,HO,CO}}, 8$; $f_{\text{CO,CC-O}} \rightarrow f_{\text{CO,OCO}}, 10 \text{ cm}^{-1}$. ^d $f_{\text{CC,CC}}, -8$; $f_{\text{CO,HC=O}}, -14$; $f_{\text{CC,HCC}}, -14$; $f_{\text{CC,CO-O}}, -8 \text{ cm}^{-1}$. ^e $f_{\text{CO-O,OCO}}, -3$; $f_{\text{CO-O,CC}}, 13$; $f_{\text{CO-O,HC-O}}, -20$; $f_{\text{CO-O,HC=O}}, -26 \text{ cm}^{-1}$.

to obtain satisfactory agreement with observation. The approximate potential energy distribution (p.e.d.) for the carbonyl vibration is not significantly modified by small changes in the C-O constant and calculation for deuterio-

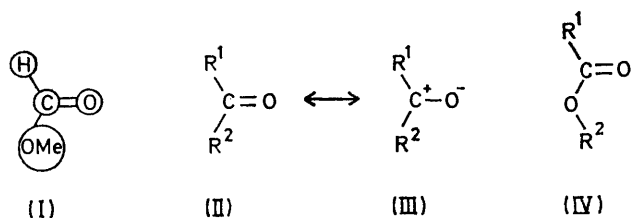
$36\sigma^* + 1754 \text{ cm}^{-1}$, but this cannot be extended to the more general equation by the use of σ_{H}^* .

¹² See e.g. W. A. Seth-Paul and A. Van Duyse, *Spectrochim. Acta*, 1972, **28**, 211; N. Fuson, M. L. Josien, and E. M. Shelton, *J. Amer. Chem. Soc.*, 1954, **76**, 2526; H. W. Thompson, R. W. Needham, and D. Jameson, *Spectrochim. Acta*, 1957, **9**, 208.

¹³ K. J. Morgan and N. Unwin, *J. Chem. Soc. (B)*, 1968, 880.

¹¹ A. J. Collings, P. F. Jackson, and K. J. Morgan, *J. Chem. Soc. (B)*, 1970, 581.

In solution regularities persist except that the frequencies for the *t*-butyl ester ($\sigma_{\text{Ba}}^{\text{t}*} - 0.3$) show low sensitivity to solvent effects and in polar solvents occur at values close to those for isopropyl formate ($\sigma_{\text{Pr}}^{\text{t}*} - 0.19$). The fit of modified Bellamy, Hallam, and Williams¹⁴



(BHW) equations, $\nu = m\nu_{\text{ref}} + d$, is good with either methyl formate or methyl acetate as the reference compound. The sensitivity of the carbonyl frequency to solvent perturbation as indicated by the gradient, m , is similar to that of methyl acetate; in common with other *t*-butyl esters,¹³ *t*-butyl formate has a significantly smaller gradient. The lack of irregularities in the solvent plots indicates that no significant perturbation arises from the postulated¹⁵ interaction of either basic solvents with the formyl hydrogen or from abnormal back-side nucleophilic solvation.

The second band in the carbonyl region of the spectra of alkyl formates is also sensitive to substituents and to solvents. The decrease in frequency accompanying increasing alkyl substitution in the alkoxy-group is similar to that of the main band except that the decrease for *t*-butyl is considerably greater. The effects of solvents on the band frequency give good modified BHW¹⁴ plots against the carbonyl frequency for methyl acetate (m ca. 1.6) suggesting that this band may also be assigned to a carbonyl vibration.

The stable configuration of esters corresponds to the *s-trans* form¹⁶ (IV) and dipole moment,¹⁷ electron diffraction,¹⁸ and microwave measurements¹⁹ establish that methyl and ethyl formates have this configuration though these methods would not be sensitive to the presence of small amounts of the isomeric *s-cis* forms. Ultrasonic relaxation measurements²⁰ have provided evidence for the existence of formates in both forms

† In methyl deuterioformate assumption²⁴ of Fermi resonance between the corresponding two bands gave an apparent carbonyl frequency of 1732 cm^{-1} ; this possibility is removed in the revised assignment and the bands are now assigned *s-cis* form, 1751 cm^{-1} , *s-trans* form, 1712 cm^{-1} , the latter being in good agreement with that calculated for the simple model.

¹⁴ L. J. Bellamy, H. E. Hallam, and R. L. Williams, *Trans. Faraday Soc.*, 1958, **54**, 1120; A. J. Collings and K. J. Morgan, *J. Chem. Soc.*, 1963, 3437.

¹⁵ N. Muller, *J. Chem. Phys.*, 1961, **36**, 359; R. Erkk and J. Jokisaari, *Z. Naturforsch.*, 1968, **23a**, 2100; R. C. Paul, S. L. Chadha, and J. L. Vashisht, *Indian J. Chem.*, 1969, **7**, 275; cf. J. D. Lambert, J. S. Clarke, J. Duke, C. L. Hicks, S. D. Lawrence, D. M. Morris, and M. G. T. Shone, *Proc. Roy. Soc.*, 1959, **A249**, 414.

¹⁶ R. J. B. Marsden and L. E. Sutton, *J. Chem. Soc.*, 1936, 1383.

¹⁷ R. J. W. Le Fevre and A. Sundaram, *J. Chem. Soc.*, 1962, 3904; E. Bock, *Canad. J. Chem.*, 1967, **45**, 2761.

showing rapid equilibration in which the *s-trans* form is the major component. I.r. measurements^{21,22} of alkyl formates have been interpreted in terms of an exclusive *s-trans* structure but recent work²³ has identified thermally sensitive skeletal bands with *cis-trans* rotational isomerism.

Assignment of a second band in the carbonyl region of the spectrum of *t*-butyl formate to the *s-cis* form was made by Oki *et al.*⁹ and supported by a wide variety of other physical measurements. Further support is provided by the solvent dependence of this band which is similar to that of other *s-cis* esters (e.g. δ -valerolactone; m 1.49). The previous failure to observe similar bands in the spectra of less heavily substituted alkyl formates may be attributed to the comparative weakness of the bands. However the band at 1796 (vap) and 1768 cm^{-1} (CCl_4) in the spectrum of methyl formate and attributed by Wilmshurst²¹ to a combination band [1433 (CH_3 sym bend) + 335 cm^{-1} (C-O bend)] can now be identified with ν_{CO} for the *s-cis* form: its solvent dependence and the occurrence of similar bands in the spectra of other alkyl formates do not appear to be compatible with the original assignment.†

In comparison with other esters the main carbonyl band in alkyl formates appears at low frequencies. This band is derived from the *s-trans* form typical for carboxylates and no electronic interactions peculiar to formates are expected. The substitution of hydrogen for alkyl is unlikely to reduce the carbonyl force constant and the cause of the low frequency may lie in the contributions of other factors to the carbonyl vibration.

Some indication of the nature of the carbonyl group vibration in methyl formate is provided by analysis of the simple tetra-atomic model (I). For this model the carbonyl frequency is largely determined by the carbonyl force constant but the vibration contains contributions from the C-O and C-H groups: the diagonal elements of the **F** matrix give an approximate p.e.d. of C=O (stretch) 73, C-O (stretch) 6, and C-H (bend) 17%. These values are generally similar to those obtained by Susi and Scherer²⁵ from a full vibrational analysis using a modified valence force field (C=O 79, C-O 14, and C-H 7%) though the presence of a number of large interaction constants in the set used by Susi and Scherer²⁵ makes difficult a direct comparison of diagonal p.e.d.s.

¹⁸ J. M. O'Gorman, W. Shand, and V. Schomaker, *J. Amer. Chem. Soc.*, 1950, **72**, 4222.

¹⁹ R. F. Curl, *J. Chem. Phys.*, 1959, **30**, 1529; J. M. Riveres and E. B. Wilson, *ibid.*, 1967, **46**, 4605.

²⁰ J. Karpovich, *J. Chem. Phys.*, 1954, **22**, 1767; D. Tabucii, *ibid.*, 1958, **28**, 1014; D. N. Hall and J. Lamb, *Trans. Faraday Soc.*, 1959, **55**, 784; K. M. Burundukov and V. F. Yakovlev, *Russ. J. Phys. Chem.*, 1968, **42**, 1141; J. Bailey and A. M. North, *Trans. Faraday Soc.*, 1968, **64**, 1499; J. Bailey, S. Walker, and A. M. North, *J. Mol. Structure*, 1970, **6**, 53.

²¹ J. K. Wilmshurst, *J. Mol. Spectroscopy*, 1957, **1**, 201.

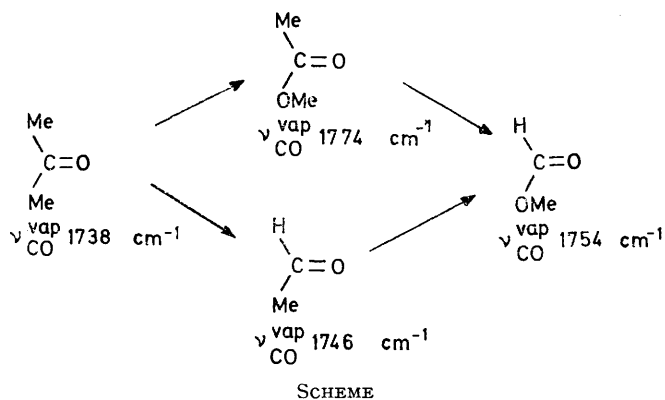
²² T. Miyazawa, *Bull. Chem. Soc. Japan*, 1961, **34**, 691; N. L. Owen and N. Sheppard, *Proc. Chem. Soc.*, 1963, 264.

²³ W. O. George, D. V. Hassid, and W. F. Maddams, *J.C.S. Perkin II*, 1972, 1029.

²⁴ H. Susi and T. Zell, *Spectrochim. Acta*, 1963, **19**, 1933.

²⁵ H. Susi and J. R. Scherer, *Spectrochim. Acta*, 1969, **25A**, 1243.

The simplicity of the tetra-atomic model for methyl formate and its similarity to those used previously for other simple carbonyl compounds^{1,11} enables some possible vibrational substituent effects to be examined. Taking acetone as reference compound it is useful to consider two sequences of structural change (Scheme).



Stepwise conversion of parameters for the model of acetone¹ to those for methyl acetate¹¹ suggests that the

nett rise in carbonyl frequency is not dependent on the carbonyl force constant but may be attributed to increased rigidity imparted by a C-O bond. Similar consequences of the introduction of a C-O bond appear in the transformation of acetaldehyde to formate but increases in the carbonyl frequency arise from coupling of C-H (bend) to C=O (stretch) and C-O (stretch). The complementary changes due to the replacement of methyl by hydrogen produce substantial mass and coupling effects which are similar for the change acetone-acetaldehyde and for acetate-formate. The largest individual changes arise from the substituent effects of hydrogen on the carbonyl force constant. In acetaldehyde this effect is greater than in formate, even so for formate the force constant is significantly higher than for acetate. Consequently the low frequency of formate with respect to acetate may be attributed to the mass and coupling effects accompanying the introduction of a hydrogen atom.

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